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INTERCALATION REACTIONS OF MONOVALENT AND DIVALENT  
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MINNEAPOLIS CORROSION RESEARCH CENTER  
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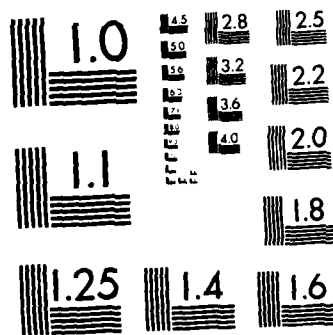
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) <b>Single Crystal <math>V_{60}13</math> positive material is being evaluated in this laboratory for the intercalation of polyvalent cations such as Li, Na Zn, Cu etc. The study involves 1) growth of <math>V_{60}13</math> single crystals, 2) the reversible behavior <math>V_{60}13</math> towards polyvalent cations, 3) evaluation of the thermodynamic EMF vs composition curves and 4) XRD and STM determination in order to evaluate any structural changes occurring in the <math>V_{60}13</math> as a result of cation intercalation.</b>											
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Intercalation Reactions of Monovalent and  
Divalent Cations in  $V_6O_{13}$  Single Crystals

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The use of  $V_6O_{13}$  as a cathode material in non-aqueous lithium secondary batteries was originally reported by Murphy, et al. in 1979 [1]. Subsequently, the  $Li/V_6O_{13}$  couple has been the subject of intense research by various groups [2-6]. From a secondary battery application, the key areas of interest for the cathode is defined by high electronic conductivity, high reversibility, high diffusivity (leading to high power densities), wide composition range (allowing high cell capacities) and minimal structural change with composition, and in this respect lithium satisfies most of the criteria. The theoretical energy density of the  $Li/V_6O_{13}$  couple is 890 Wh/kg, which is considerably greater when compared to some of the other intercalation cathodes such as  $TiS_2$ ). This value together with the relative ease of manufacture of  $V_6O_{13}$  makes it a highly promising cathode material in rechargeable lithium batteries. However, the safety and cycle life of ambient temperature secondary lithium batteries, usually associated with the high reactivity of elemental lithium anode, poses a serious problem. This may be overcome, however, by finding alternative anodes which may be more stable and have reasonable energy densities.

So far there is no report in the open literature on intercalation studies pertaining to cations other than lithium. It would be highly desirable if  $V_6O_{13}$  was reversible to other cations from a battery technology viewpoint.

Previous emphasis has been placed on studying polycrystalline  $V_6O_{13}$ . In order to establish fundamental properties, single crystals need to be investigated.

In this laboratory, the process for growing large single crystals has now been well established. The first part of the investigation was to reproduce the work already performed for  $Li^+$  insertion into the single crystal material. This was completed successfully by utilizing cells made of a lithium anode, a  $V_6O_{13}$  single crystal as cathode and  $LiClO_4$  dissolved in propylene carbonate (PC) as the electrolyte. Thermodynamic EMF vs composition curves obtained by titrating lithium ions into the cathode were consistent with literature values.

The work has now been extended to include anodes such as Zn, Cu, Mg, Na and Ca. The initial results indicate that Zn and Cu may be inserted and removed reversibly from the  $V_6O_{13}$  cathode.

Acknowledgement

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References

1. D.W. Murphy, P.A. Christian, F.J. DiSalvo and J.N. Carides, J. Electrochem. Soc. **126**, (1979), 497.
2. D.W. Murphy, P.A. Christian, F.J. DiSalvo J.N. Carides, and J.V. Waszczak, *ibid.* **128** (1981) 2053.
3. P.C. Spurdens, J. Drennen, J.R. Owen, B.C.H. Steel, J.M. Gonzales-Calbert and D.A. Jefferson, Solid State Ionics, **5** (1981) 335.
4. J.R. Owen, J. Drennen, G.E. Lagos, P.C. Spurdens and B.C.H. Steele, Solid State Ionics, **5** (1981), 343.
5. K. West, B. Zachau-Christiansen, T. Jacobsen and S. Atlung, J. Power Sources, **14** (1985) 235.
6. P.C. Spurdens and B.C.H. Steele, Solid State Ionics, **21** (1981) 151.

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